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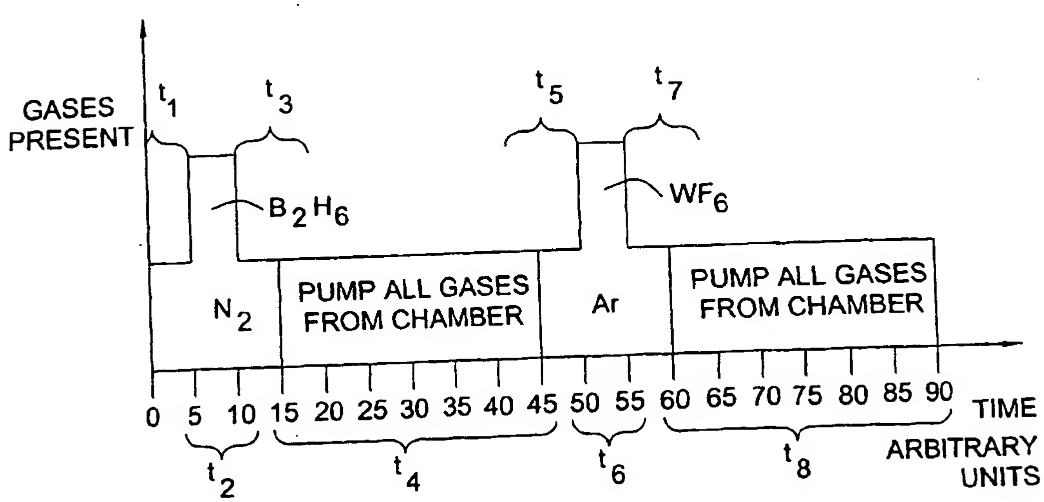

(57) Abstract: A method and system to form a refractory metal layer over a substrate includes introduction of a reductant, such as PH3 or B2H6, followed by introduction of a tungsten containing compound, such as WF6, to form a tungsten layer. It is believed that the reductant reduces the fluorine content of the tungsten layer while improving the step coverage and resistivity of the tungsten layer. It is believed that the improved characteristics of the tungsten film are attributable to the chemical affinity between the reductants and the tungsten containing compound. The chemical affinity provides better surface mobility of the adsorbed chemical species and better reduction of WF6 at the nucleation stage of the tungsten layer. The method can further include sequentially introducing a reductant, such as PH3 or B2H6, and a tungsten containing compound to deposit a tungsten layer. The formed tungsten layer can be used as a nucleation layer followed by bulk deposition of a tungsten layer utilizing standard CVD techniques. Alternatively, the formed tungsten layer can be used to fill an aperture.

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METHOD AND APPARATUS FOR DEPOSITING TUNGSTEN AFTER SURFACE TREATMENT TO IMPROVE FILM CHARACTERISTICS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims benefit of United States Provisional Patent Application Serial Number 60/305,765, filed July 16, 2001, which is herein incorporated by reference.

BACKGROUND OF THE INVENTION

Field of the Invention

[0002] Embodiments of the invention relate to the processing of semiconductor substrates. More particularly, embodiments of the invention relate to improvements in the process of depositing refractory metal layers on semiconductor substrates.

Description of the Related Art

[0003] The semiconductor processing industry continues to strive for larger production yields while increasing the uniformity of layers deposited on substrates having larger surface areas. These same factors in combination with new materials also provide higher density of circuits per unit area of the substrate. As circuit density increases, the need for greater uniformity and process control regarding layer thickness rises. As a result, various technologies have been developed to deposit layers on substrates in a cost-effective manner, while maintaining control over the characteristics of the layer. Chemical Vapor Deposition (CVD) is one of the most common deposition processes employed for depositing layers on a substrate. CVD is a flux-dependent deposition technique that requires precise control of the substrate temperature and precursors introduced into the processing chamber in order to produce a desired layer of uniform thickness. These requirements become more critical as substrate size increases (e.g., from 200 mm diameter substrates to 300 mm substrates), creating a need for more complexity in chamber design and gas flow technique to maintain adequate uniformity.

[0004] A variant of CVD that demonstrates superior step coverage compared to CVD, is Atomic Layer Deposition (ALD). ALD is based upon Atomic Layer Epitaxy (ALE) that was employed originally to fabricate electroluminescent displays. ALD

employs chemisorption to deposit a saturated monolayer of reactive precursor molecules on a substrate surface. This is achieved by alternatingly pulsing an appropriate reactive precursor into a deposition chamber. Each injection of a reactive precursor is separated by an inert gas purge to provide an adsorbed atomic layer to previously deposited layers to form a uniform layer on the substrate. The cycle is repeated to form the layer to a desired thickness. A drawback with ALD techniques is that the deposition rate is much lower than typical CVD techniques by at least one order of magnitude.

[0005] Formation of film layers at a high deposition rate while providing adequate step coverage are conflicting characteristics often necessitating sacrificing one to obtain the other. This conflict is true particularly when refractory metal layers are deposited to cover apertures or vias during formation of contacts that interconnect adjacent metallic layers separated by dielectric layers. Historically, CVD techniques have been employed to deposit conductive material such as refractory metals in order to inexpensively and quickly fill vias. Due to the increasing density of semiconductor circuitry, tungsten has been used based upon superior step coverage to fill these high aspect ratio structures. As a result, deposition of tungsten employing CVD techniques enjoys wide application in semiconductor processing due to the high throughput of the process and good step coverage.

[0006] Depositing tungsten by traditional CVD methods, however, is attendant with several disadvantages. For example, blanket deposition of a tungsten layer on a semiconductor wafer is time-consuming at temperatures below 400°C. The deposition rate of tungsten may be improved by increasing the deposition temperature between approximately 500°C to 550°C; however, temperatures in this higher range may compromise the structural and operational integrity of the underlying portions of the integrated circuit being formed. Use of tungsten has also complicated photolithography steps during the manufacturing process as it results in a relatively rough surface having a reflectivity of 20% or less than that of a silicon substrate. Finally, tungsten has proven difficult to deposit uniformly. Variance in film thickness of greater than 1% has been

shown, thereby causing poor control of the resistivity of the layer. Several prior attempts to overcome the aforementioned drawbacks have been attempted.

[0007] For example, in United States Patent Number 5,028,565 to Chang et al., which is assigned to the assignee of the present invention, a method is disclosed to improve, inter alia, uniformity of tungsten layers by varying the deposition chemistry. The method includes, in pertinent part, formation of a nucleation layer over an intermediate barrier layer before depositing the tungsten layer via bulk deposition. The nucleation layer is formed from a gaseous mixture of tungsten hexafluoride, hydrogen, silane and argon. The nucleation layer is described as providing a layer of growth sites to promote uniform deposition of a tungsten layer thereon. The benefits provided by the nucleation layer are described as being dependent upon the barrier layer present. For example, were the barrier layer formed from titanium nitride, the tungsten layer's thickness uniformity is improved as much as 15%. Were the barrier layer formed from sputtered tungsten or sputtered titanium tungsten, the benefits provided by the nucleation layer are not as pronounced.

[0008] A need exists, therefore, to provide techniques to improve the characteristics of refractory metal layers deposited on semiconductor substrates.

SUMMARY OF THE INVENTION

[0009] A method and system to form a refractory metal layer over a substrate includes introduction of a reductant, such as PH_3 or B_2H_6, followed by introduction of a tungsten containing compound, such as WF_6, to form a tungsten layer. It is believed that the reductant reduces the fluorine content of the tungsten layer while improving the step coverage and resistivity of the tungsten layer. It is believed that the improved characteristics of the tungsten film are attributable to the chemical affinity between the reductants and the tungsten containing compound. The chemical affinity provides better surface mobility of the adsorbed chemical species and better reduction of WF_6 at the nucleation stage of the tungsten layer.

[0010] The method can further include sequentially introducing a reductant, such as PH_3 or B_2H_6, and a tungsten containing compound to deposit a tungsten layer. The formed tungsten layer can be used as a nucleation layer followed by bulk deposition of a tungsten layer utilizing standard CVD techniques. Alternatively, the formed tungsten layer can be used to fill an aperture.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] Figure 1 is a perspective view of one embodiment of a semiconductor processing system in accordance with the present invention

[0012] Figure 2 is a schematic cross-sectional view of one embodiment of the processing chambers shown above in Figure 1.

[0013] Figure 3 is a schematic cross-sectional view of a substrate showing one possible mechanism of adsorption of a reductant over a substrate during sequential deposition.

[0014] Figure 4 is a schematic cross-sectional view of a substrate showing one possible mechanism of adsorption of a refractory metal containing compound over the substrate after introduction of the reductant.

[0015] Figure 5 is a graphical representation showing the concentration of gases present in a processing chamber, such as processing chamber as shown above in Figure 2.

[0016] Figure 6 is a graphical representation showing the relationship between the number of ALD cycles and the thickness of a layer formed on a substrate employing sequential deposition techniques, in accordance with the present invention.

[0017] Figure 7 is a graphical representation showing the relationship between the number of sequential deposition cycles and the resistivity of a layer formed on a substrate employing sequential deposition techniques, in accordance with the present invention.

[0018] Figure 8 is a graphical representation showing the relationship between the deposition rate of a layer formed on a substrate employing sequential deposition techniques and the temperature of the substrate.

[0019] Figure 9 is a graphical representation showing the relationship between the resistivity of a layer formed on a substrate employing sequential deposition techniques and the temperature of the substrate, in accordance with the present invention.

[0020] Figure 10 is a schematic cross-sectional view of one embodiment of a patterned substrate having a nucleation layer formed thereon employing sequential deposition techniques, in accordance with the present invention.

[0021] Figure 11 is a schematic cross-sectional view of one embodiment of the substrate, shown above in Figure 10, with a refractory metal layer formed atop of the nucleation layer employing CVD, in accordance with the present invention.

[0022] Figure 12 is a graphical representation showing the concentration of gases present in a processing chamber, such as the processing chamber as shown above in Figure 2, in accordance with an alternative embodiment of the present invention.

[0023] Figure 13 is a graphical representation showing the concentration of gases present in a processing chamber, such as processing chamber as shown above in Figure 2, in accordance with an alternative embodiment of the present invention.

[0024] Figure 14 is a graphical representation showing the fluorine content versus depth of a refractory metal layer formed on a substrate employing ALD, either Ar or N_2 being a carrier gas.

[0025] Figure 15 is a graphical representation showing the fluorine content versus depth of a refractory metal layer formed on a substrate employing ALD with H_2 being a carrier gas.

[0026] Figure 16 is a schematic cross-sectional view of one embodiment of a substrate shown above in Figures 3 and 4 upon which a layer of either PH_3 or B_2H_6 is

disposed between a substrate and a tungsten layer, in accordance with one embodiment of the present invention.

[0027] Figure 17 is a graphical representation showing the concentration of gases present in a processing chamber, such as processing chamber as shown above in Figure 2, in accordance with one embodiment of the present invention.

[0028] Figure 18 is a schematic cross-sectional view of one embodiment of a substrate shown above in Figures 3 and 4 in which a titanium-containing layer is deposited between a substrate and a layer of either PH_3 or B_2H_6, in accordance with the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

[0029] Referring to Figure 1, an exemplary wafer processing system includes one or more processing chambers 12 and 14 disposed in a common work area 16 surrounded by a wall 18. Processing chambers 12 and 14 are in data communication with a controller 22 that is connected to one or more monitors, shown as 24 and 26. The monitors typically display common information concerning the process associated with processing chambers 12 and 14. One of the monitors 26 is mounted on wall 18, with the remaining monitor 24 being disposed in work area 16. Operational control of processing chambers 12 and 14 may be achieved by the use of a light pen, associated with one of the monitors 24 and 26, to communicate with controller 22. For example, light pen 28 is associated with monitor 24 and facilitates communication with controller 22 through monitor 24. Light pen 39 facilitates communication with controller 22 through monitor 26.

[0030] Referring both to Figures 1 and 2, each of processing chambers 12 and 14 includes a housing 30 having a base wall 32, a cover 34 disposed opposite to base wall 32, and a sidewall 36 extending therebetween. Housing 30 defines a chamber 37, and a pedestal 38 is disposed within processing chamber 37 to support a substrate 42, such as a semiconductor wafer. Pedestal 38 may be mounted to move between cover 34

and base wall 32, using a displacement mechanism (not shown), but the position thereof is typically fixed. Supplies of processing gases 39a, 39b and 39c are in fluid communication with processing chamber 37 via a showerhead 40. Regulation of the flow of gases from supplies 39a, 39b and 39c is effectuated via flow valves 41.

[0031] Depending on the specific process, substrate 42 may be heated to a desired temperature prior to layer deposition via a heater embedded within pedestal 38. For example, pedestal 38 may be resistively heated by applying an electric current from AC power supply 43 to heater element 44. Substrate 42 is, in turn, heated by pedestal 38, and can be maintained within a desired process temperature range of, for example, about 20°C to about 750°C. A temperature sensor 46, such as a thermocouple, is also embedded in wafer support pedestal 38 to monitor the temperature of pedestal 38 in a conventional manner. For example, the measured temperature may be used in a feedback loop to control the electrical current applied to heater element 44 by power supply 43 such that the substrate temperature can be maintained or controlled at a desired temperature that is suitable for the particular process application. Optionally, pedestal 38 may be heated using radiant heat (not shown). A vacuum pump 48 is used to evacuate processing chamber 37 and to help maintain the proper gas flows and pressure inside processing chamber 37.

[0032] Referring to Figures 1 and 2, one or both of processing chambers 12 and 14, discussed above may operate to deposit refractory metal layers on the substrate employing sequential deposition techniques. One example of sequential deposition techniques in accordance with the present invention includes atomic layer deposition (ALD). The term "substrate" as used herein includes the substrate, such as semiconductor substrates and glass substrates, as well as layers formed thereover, such as dielectric layers (*i.e.*, SiO_2) and barrier layers (*i.e.*, titanium, titanium nitride and the like).

[0033] Not wishing to be bound by theory, Figure 3 is a schematic cross-sectional view of a substrate showing one possible mechanism of adsorption of a reductant over

a substrate during sequential deposition. The terms "adsorption" or "adsorb" as used herein are defined to include chemisorption, physisorption, or any attractive and/or bonding forces which may be at work and/or which may contribute to the bonding, reaction, adherence, or occupation of a portion of an exposed surface of a substrate structure. During the sequential deposition technique, in accordance with the present invention, a batch of a first processing gas, in this case "Aa_x," results in a layer of "A" being deposited on substrate 42 having a surface of ligand "a" exposed to processing chamber 37. Layer "A" may be a monolayer, more than a monolayer, or less than a monolayer. Thereafter, a purge gas enters processing chamber 37 to purge gas "Aa_x," which has not been incorporated into the layer of A. Figure 4 is a schematic cross-sectional view of a substrate showing one possible mechanism of adsorption of a refractory metal containing compound over the substrate after introduction of the reductant. After purging gas "Aa_x" from processing chamber 37, a second batch of processing gas, "Bb_y," is introduced into processing chamber 37. The "a" ligand present on the substrate surface reacts with the "b" ligand and "B" atom, releasing molecules, for example, "ab" and "aA," which move away from substrate 42 and are subsequently pumped from processing chamber 37. In this manner, a surface comprising a layer of B compound remains upon substrate 42 and exposed to processing chamber 37, shown in Figure 4. The composition of the layer of B compound may be a monolayer or less of atoms typically formed employing ALD techniques. In other embodiments, more than a monolayer of B compound may be formed during each cycle. Alternatively, the layer of compound B may include a layer of multiple atoms (i.e. other atoms besides atoms of B). In such a case, the first batch and/or the second batch of processing gases may include a mixture of process gases, each of which has atoms that would adhere to substrate 42. The process proceeds cycle after cycle, until the desired thickness is achieved.

[0034] Referring to both Figures 3 and 4, although any type of processing gas may be employed, in the present example, the reductant "Aa_x" may comprise B_2H_6 or PH_3 and the refractory metal containing compound, Bb_y, may comprise WF_6. Some

possible reactions are shown below in reference to chemical reaction (1) and chemical reaction (2).

(1) B_2H_6 (g) + WF_6 (g) --> W (s) + $2BF_3$ (g)

(2) PH_3 (g) + WF_6 (g) --> W (s) + PF_3 (g)

Other by-products include but are not limited to H_2, HF, F_2. Other reactions are also possible, such as decomposition reactions. In other embodiments, other reductants may be used, such as SiH_4. Similarly, in other embodiments, other tungsten containing gases may be used, such as $W(CO)_6$.

[0035] The purge gas includes Ar, He, N_2, H_2, other suitable gases, and combinations thereof. One or more purge gas may be used. Figure 5 is a graphical representation of one embodiment of gases present in a processing chamber utilizing two purge gases Ar and N_2. Each of the processing gases was flowed into processing chamber 37 with a carrier gas, which in this example was one of the purge gases. WF_6 is introduced with Ar and B_2H_6 is introduced with N_2. It should be understood, however, that the purge gas may differ from the carrier gas, discussed more fully below. One cycle of the ALD technique in accordance with the present invention includes flowing the purge gas, N_2, into processing chamber 37 during time t_1, which is approximately about 0.01 to about 15 seconds before B_2H_6 is flowed into processing chamber 37. During time t_2, the processing gas B_2H_6 is flowed into processing chamber 37 for a time in the range of about 0.01 to about 15 seconds, along with a carrier gas, which in this example is N_2. After about 0.01 to about 15 seconds have lapsed, the flow of B_2H_6 terminates and the flow of N_2 continues during time t_3 for an additional time in the range of about 0.01 to about 15 seconds, purging the processing chamber of B_2H_6. During time t_4 which lasts approximately about 0 to about 30 seconds, processing chamber 37 is pumped so as to remove most, if not all, gases. After pumping of process chamber 37, the carrier gas Ar is introduced for a time in the range of about 0.01 to about 15 seconds during time t_5, after which time the process gas WF_6 is introduced into processing chamber 37, along with the carrier gas Ar during time t_6. The time t_6 lasts

between about 0.01 to about 15 seconds. The flow of the processing gas WF_6 into processing chamber 37 is terminated approximately about 0.01 to about 15 seconds after it commenced. After the flow of WF_6 into processing chamber 37 terminates, the flow of Ar continues for an additional time in the range of 0.01 to 15 seconds, during time t_7. Thereafter, processing chamber 37 is pumped so as to remove most, if not all, gases therein, during time t_8. As before, time t_8 lasts approximately about 0 to about 30 seconds, thereby concluding one cycle of the sequential deposition technique, in accordance with the present invention. The cycle may be repeated to deposit a tungsten layer to a desired thickness.

[0036] The benefits of employing the sequential deposition technique are many fold, including flux-independence of layer formation that provides uniformity of deposition independent of the size of a substrate. For example, the measured difference of the layer uniformity and thickness measured between a 200 mm substrate and a 300 mm substrate deposited in the same chamber is negligible. This is due to the self-limiting characteristics of the sequential deposition techniques. Further, this technique contributes to improved step coverage over complex topography.

[0037] In addition, the thickness of the layer B, shown in Figure 4, may be easily controlled while minimizing the resistance of the same by employing sequential deposition techniques. With reference to Figure 6, it is seen in the slope of line 50 that the thickness of the tungsten layer B is proportional to the number of cycles employed to form the same. The resistivity of the tungsten layer, however, is relatively independent of the thickness of the layer, as shown by the slope of line 52 in Figure 7. Thus, employing sequential deposition techniques, the thickness of a refractory metal layer maybe easily controlled as a function of the cycling of the process gases introduced into the processing chamber with a negligible effect on the resistivity.

[0038] Figure 8 is a graphical representation showing the relationship between the deposition rate of a layer formed on a substrate employing sequential deposition techniques and the temperature of the substrate. Control of the deposition rate was

found to be dependent upon the temperature of substrate 42. As shown by the slope of line 54, increasing the temperature of substrate 42 increased the deposition rate of the tungsten layer B. The graph shows that less than a monolayer, a monolayer, or more than a monolayer of a tungsten layer may be formed depending on the substrate temperature utilized. For example, at 56, the deposition rate is shown to be approximately 2 Å/cycle at 250°C. However at point 58 the deposition rate is approximately 5 Å/cycle at a temperate of 450°C. The resistivity of the tungsten layer, however, is virtually independent of the layer thickness, as shown by the slope of curve 59, shown in Figure 9. As a result, the deposition rate of the tungsten layer may be controlled as a function of temperature without compromising the resistivity of the same. However, it may be desirable to reduce the time necessary to deposit an entire layer of a refractory metal.

[0039] To that end, a bulk deposition of the refractory metal layer may be included in the deposition process. Typically, the bulk deposition of the refractory metal occurs after the nucleation layer is formed in a common processing chamber. Specifically, in the present example, nucleation of a tungsten layer occurs in chamber 12 employing the sequential deposition techniques discussed above, with substrate 42 being heated in the range of about 200°C to about 400°C, and processing chamber 37 being pressurized in the range of about 1 to about 10 Torr. A nucleation layer 60 of approximately about 120 to about 200 Å is formed on a patterned substrate 42, shown in Figure 10. Nucleation layers of about 100 Å or less, about 50 Å or less, or about 25 Å or less have also been found to be effective in providing good step coverage over apertures having an aspect ratio of about 6:1 or greater. As shown, substrate 42 includes a barrier layer 61 and a patterned layer having a plurality of vias 63. The nucleation layer is formed adjacent to the patterned layer covering vias 63. As shown, forming nucleation layer 60 employing ALD techniques provides good step coverage. In another embodiment, sequential deposition techniques may be performed for both nucleation and bulk deposition. In still another embodiment, to decrease the time required to form a complete layer of tungsten, a bulk deposition of tungsten onto nucleation layer 60 occurs using CVD techniques, while substrate 42 is disposed in the

same processing chamber 12, shown in Figure l. The bulk deposition may be performed using recipes well known in the art. In this manner, a tungsten layer 65 providing a complete plug fill is achieved on the patterned layer with vias having aspect ratios of approximately 6:1, shown in Figure 11.

[0040] In an alternative embodiment, a bifurcated deposition process may be practiced in which nucleation of the refractory metal layer occurs in a chamber that is different from the chamber in which the remaining portion of the refractory metal layer is formed. Specifically, in the present example, nucleation of a tungsten layer occurs in chamber 12 employing the sequential deposition techniques, such as ALD, discussed above. To that end, substrate 42 is heated in the range of about 200°C to about 400°C and chamber 37 is pressurized in the range of about 1 to about 10 Torr. A nucleation layer 60 of approximately 120 to 200 Å is formed on a patterned substrate 42, shown in Figure 10. Nucleation layers of about 100 Å or less, about 50 Å or less, or about 25 Å or less have also been found to be effective in providing good step coverage over apertures having an aspect ratio of about 6:1 or greater. As shown, substrate 42 includes a barrier layer 61 and a patterned layer having a plurality of vias 63. The nucleation layer is formed adjacent to the patterned layer covering the vias 63. As shown, forming the nucleation layer 60 employing sequential deposition techniques provides improved step coverage.

[0041] In one embodiment, sequential deposition techniques are employed for bulk deposition of tungsten onto nucleation layer 60 occurs while substrate 42 is disposed in processing chamber 14, shown in Figure 1. The bulk deposition maybe performed using recipes disclosed herein. In another embodiment, CVD techniques are employed for bulk deposition of tungsten onto nucleation layer 60 occurs while substrate 42 is disposed in processing chamber 14, shown in Figure 1. The bulk deposition maybe performed using recipes well known in the art. Whether sequential deposition or CVD deposition techniques are employed, a tungsten layer 65 providing a complete plug fill is achieved on the patterned layer with vias having aspect ratios of approximately 6:1, shown in Figure 11. Implementing the bifurcated deposition process discussed above

may decrease the time required to form a tungsten layer having improved characteristics. Utilizing CVD deposition techniques for bulk deposition may further increase throughput.

[0042] As mentioned above, in an alternate embodiment of the present invention, the carrier gas may differ from the purge gas, as shown in Figure 12. The purge gas, which is introduced at time intervals t_1, t_3, t_5 and t_7 comprises Ar. The carrier gas, which is introduced at time intervals t_2 and t_6, comprises of N_2. Thus, at time interval t_2 the gases introduced into the processing chamber include a mixture of B_2H_6 and N_2, and a time interval t_6, the gas mixture includes WF_6 and N_2. The pump process during time intervals t_4 and t_8 is identical to the pump process discussed above with respect to Figure 5. In yet another embodiment, shown in Figure 13, the carrier gas during time intervals t_2 and t_6 comprises H_2, with the purge gas introduced at time intervals t_1, t_3, t_5 and t_7 comprising of Ar. The pump processes at time intervals t_4 and t_8 are as discussed above, As a result, at time interval t_2 the gas mixture introduced into processing chamber 37 comprises of B_2H_6 and H_2, and WF_6, and H_2 at time interval t_6.

[0043] An advantage realized by employing the H_2 carrier gas is that the stability of the tungsten layer B may be improved. Specifically, by comparing curve 66 in Figure 14 with curve 68 in Figure 15, it is seen that the concentration of fluorine in the nucleation layer 60, shown in Figure 10, is much less when H_2 is employed as the carrier gas, as compared with use of N_2 or Ar as a carrier gas.

[0044] Referring to both Figures 14 and 15, the apex and nadir of curve 66 show that the fluorine concentration reaches levels in excess of 1×10^{21} atoms per cubic centimeter and only as low as just below 1×10^{19} atoms per cubic centimeter. Curve 68, however, shows that the fluorine concentration is well below 1×10^{21} atoms per cubic centimeter at the apex and well below 1×10^{17} atoms per cubic centimeter at the nadir. Thus, employing H_2 as the carrier gas provides a much more stable film, i.e., the probability of fluorine diffusing into the substrate, or adjacent layer is reduced. This also reduces the resistance of the refractory metal layer by avoiding the formation of a

metal fluoride that may result from the increased fluorine concentration. Thus, the stability of the nucleation layer, as well as the resistivity of the same, may be controlled as a function of the carrier gas employed. This is also true when a refractory metal layer is deposited entirely employing ALD techniques, i.e., without using other deposition techniques, such as CVD.

[0045] In addition, adsorbing a layer 70, shown in Figure 16, of either PH_3 or B_2H_6 prior to introduction of the tungsten containing compound forms a tungsten layer 72 with reduced fluorine content, improved step coverage, and improved resistivity. This was found to be the case where the tungsten containing compound is introduced over a layer of PH_3 or B_2H_6 employing sequential deposition techniques or employing standard CVD techniques using either tungsten hexafluoride, WF_6, and silane, SiH_4, or tungsten hexafluoride, WF_6, and molecular hydrogen, H_2, chemistries. The improved characteristics of the tungsten film are believed to be attributable to the chemical affinity between the PH_3 or B_2H_6 layer and the WF_6 layer. This provides better surface mobility of the adsorbed chemical species and better reduction of WF_6 at the nucleation stage of the tungsten layer. This has proven beneficial when depositing a tungsten layer adjacent to a titanium containing adhesion layer formed from titanium, Ti, or titanium nitride, TiN. Layer 70 is preferably a monolayer, but in other embodiments may be less than or more than a monolayer. Layer 70 in the film stack, shown in Figure 16, shows the formation of the tungsten layer 72. It is understood that layer 70 may or may not be consumed during formation of the tungsten layer 72. It is also understood that a plurality of layers 70 and tungsten layers 72 may be deposited to form a tungsten layer to a desired thickness. As shown, layer 70 is deposited on substrate 74 that includes a wafer 76 that may be formed from any material suitable for semiconductor processing, such as silicon. One or more layers, shown as layer 74, may be present on wafer 76. Layer 78 may be formed from any suitable material, included dielectric or conductive materials. Layer 78 includes a void 80, exposing a region 82 of wafer 76.

[0046] Figure 18 is a detailed cross-sectional view of a substrate in which a titanium-containing adhesion layer is formed between a substrate and a layer of either PH_3 or

B_2H_6 during the fabrication of a W layer adjacent to the titanium-containing adhesion layer. The titanium-containing adhesion layer may be formed employing standard CVD techniques. In one embodiment, the titanium-containing adhesion layer is formed employing sequential deposition techniques. To that end, processing gas Aa_x is selected from the group including H_2, B_2H_6, SiH_4 and NH_3. Processing gas Bb_y is a titanium-containing gas selected from the group that includes TDMAT, TDEAT and $TiCl_4$. Also, Ar and N_2 purge gases are preferably employed, although other purge gas may be used.

[0047] Referring to Figures 2 and 17, each of the processing gases is flowed into processing chamber 37 with a carrier gas, which in this example, is one of the purge gases. It should be understood, however, that the purge gas may differ from the carrier gas, discussed more fully below. One cycle of the sequential deposition technique, in accordance with the present invention, includes flowing a purge gas into processing chamber 37 during time t_1 before the titanium-containing gas is flowed into processing chamber 37. During time t_2, the titanium-containing processing gas is flowed into the processing chamber 37, along with a carrier gas. After t_2 has lapsed, the flow of titanium-containing gas terminates and the flow of the carrier gas continues during time t_3, purging the processing chamber of the titanium-containing processing gas. During time t_4, the processing chamber 37 is pumped so as to remove all gases. After pumping of process chamber 37, a carrier gas is introduced during time t_5, after which time the reducing process gas is introduced into the processing chamber 37 along with the carrier gas, during time t_6. The flow of the reducing process gas into processing chamber 37 is subsequently terminated. After the flow of reducing process gas into processing chamber 37 terminates, the flow of carrier gas continues, during time t_7. Thereafter, processing chamber 37 is pumped so as to remove all gases therein, during time t_8, thereby concluding one cycle of the sequential deposition technique in accordance with the present invention. The aforementioned cycle is repeated multiple times until titanium-containing layer reaches a desired thickness. For example, in reference to Figure 18, after TiN layer 84 reaches a desired thickness, layer 86, in this example formed from PH_3 or B_2H_6, is deposited adjacent thereto employing sequential

deposition techniques, as discussed above. Thereafter, a layer of tungsten 88, shown in Figure 18, is disposed adjacent to layer 86 using the sequential deposition technique or standard CVD techniques, both of which are discussed above. Layer 86 is preferably a monolayer, but in other embodiments may be less than or more than a monolayer. Layer 86 in the film stack, shown in Figure 18, shows the formation of the tungsten layer 88. It is understood that layer 86 may or may not be consumed during formation of the tungsten layer 88. It is also understood that a plurality of layers 86 and tungsten layers 66 may be deposited to form a tungsten layer to a desired thickness. If desired, a copper layer maybe deposited atop of tungsten layer 88. In this manner, tungsten may function as a barrier layer.

[0048] Referring again to Figure 2, the process for depositing the tungsten layer may be controlled using a computer program product that is executed by controller 22. To that end, controller 22 includes a central processing unit (CPU) 90, a volatile memory, such as a random access memory (RAM) 92 and permanent storage media, such as a floppy disk drive for use with a floppy diskette, or hard disk drive 94. The computer program code can be written in any conventional computer readable programming language; for example, 68000 assembly language, C, C++, Pascal, Fortran and the like. Suitable program code is entered into a single file, or multiple files, using a conventional text editor and stored or embodied in a computer-readable medium, such as hard disk drive 94. If the entered code text is in a high level language, the code is compiled and the resultant compiler code is then linked with an object code of precompiled Windows® library routines. To execute the linked and compiled object code, the system user invokes the object code, causing the CPU 90 to load the code in RAM 92. The CPU 90 then reads and executes the code to perform the tasks identified in the program.

[0049] Although the invention has been described in terms of specific embodiments, one skilled in the art will recognize that various changes to the reaction conditions, i.e., temperature, pressure, film thickness and the like can be substituted and are meant to be included herein. Additionally, while the bifurcated deposition process has been

described as occurring in a common system, the bulk deposition may occur in a processing chamber of a mainframe deposition system that is different from the mainframe deposition system in which the processing chamber is located that is employed to deposit the nucleation layer. Finally, other refractory metals may be deposited, in addition to tungsten, and other deposition techniques may be employed in lieu of CVD. For example, physical vapor deposition (PVD) techniques, or a combination of both CVD and PVD techniques may be employed. The scope of the invention should not be based upon the foregoing description. Rather, the scope of the invention should be determined based upon the claims recited herein, including the full scope of equivalents thereof.

Claims:

1. A method of sequential deposition of a tungsten nucleation layer over a substrate in a processing chamber, comprising:

introducing a reductant selected from a group including of PH_3 and B_2H_6, and

introducing a tungsten containing compound.

2. The method of claim 1, wherein the nucleation layer is formed over a titanium-containing layer.

3. The method of claim 1, wherein a bulk tungsten layer is formed over the nucleation layer.

4. The method of claim 3, wherein the bulk tungsten layer is formed by sequential deposition.

5. The method of claim 3, wherein the bulk tungsten layer is formed by chemical vapor deposition.

6. The method of claim 3, wherein the bulk tungsten layer is formed by physical vapor deposition.

7. The method of claim 3, wherein the nucleation layer and the bulk tungsten layer are formed in a common processing chamber.

8. The method of claim 3, wherein the nucleation layer and the bulk tungsten layer are formed in separate processing chambers.

9. The method of claim 2, wherein the titanium-containing layer and the nucleation layer are formed in separate processing chambers.

10. A method of depositing a tungsten layer over a substrate in a processing chamber, comprising:

adsorbing a layer over the substrate comprising a compound selected from a group including of PH_3 and B_2H_6; and

introducing a tungsten containing compound to form a tungsten layer.

11. The method of claim 10, wherein introducing a tungsten containing compound comprises introducing a tungsten containing compound in a sequential deposition technique.

12. The method of claim 10, wherein introducing a tungsten containing compound comprising introducing a tungsten containing compound in a chemical vapor deposition technique.

13. The method of claim 10, wherein the adsorbed layer is formed over a titanium containing layer.

14. The method of claim 10, wherein adsorbing a layer and introducing a tungsten containing compound are performed in a common processing chamber.

15. The method of claim 10, wherein adsorbing a layer and introducing a tungsten containing compound are performed in separate processing chambers.

16. A processing system for a substrate, comprising:

a body defining a processing chamber;

a holder disposed within the processing chamber to support the substrate;

a gas delivery system in fluid communication with the processing chamber;

a controller in electrical communication with the gas delivery system; and

a memory in data communication with the controller, the memory comprising a

computer-readable medium having a computer-readable program embodied therein, the computer-readable program including a set of instructions for introducing a reductant selected from a group including of PH_3 and B_2H_6 and introducing a tungsten containing compound to form a nucleation layer.

17. The processing system of claim 16, wherein the computer-readable program includes a second set of instructions to form a bulk tungsten layer over the nucleation layer.

18. The processing system of claim 16, further comprising:

a second body defining a second processing chamber;

wherein the controller is in electrical communication with the second body; and

wherein the second set of instructions control formation of the bulk tungsten layer in the second body.

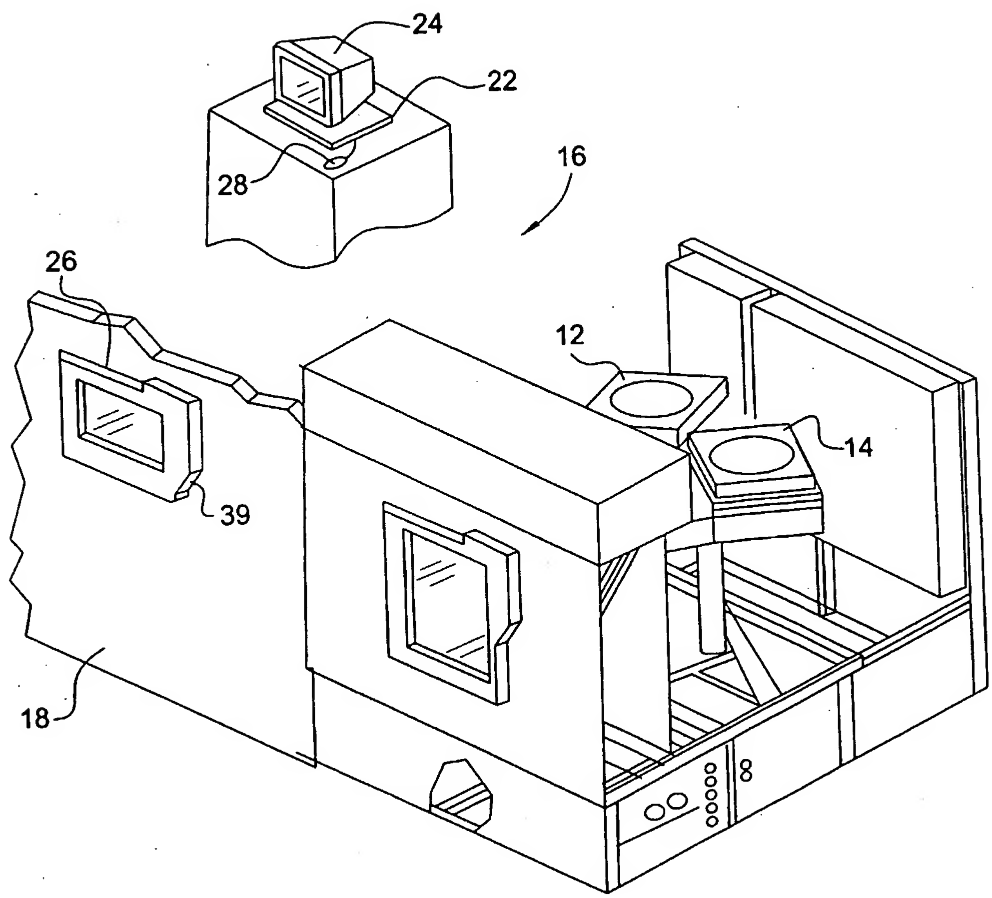
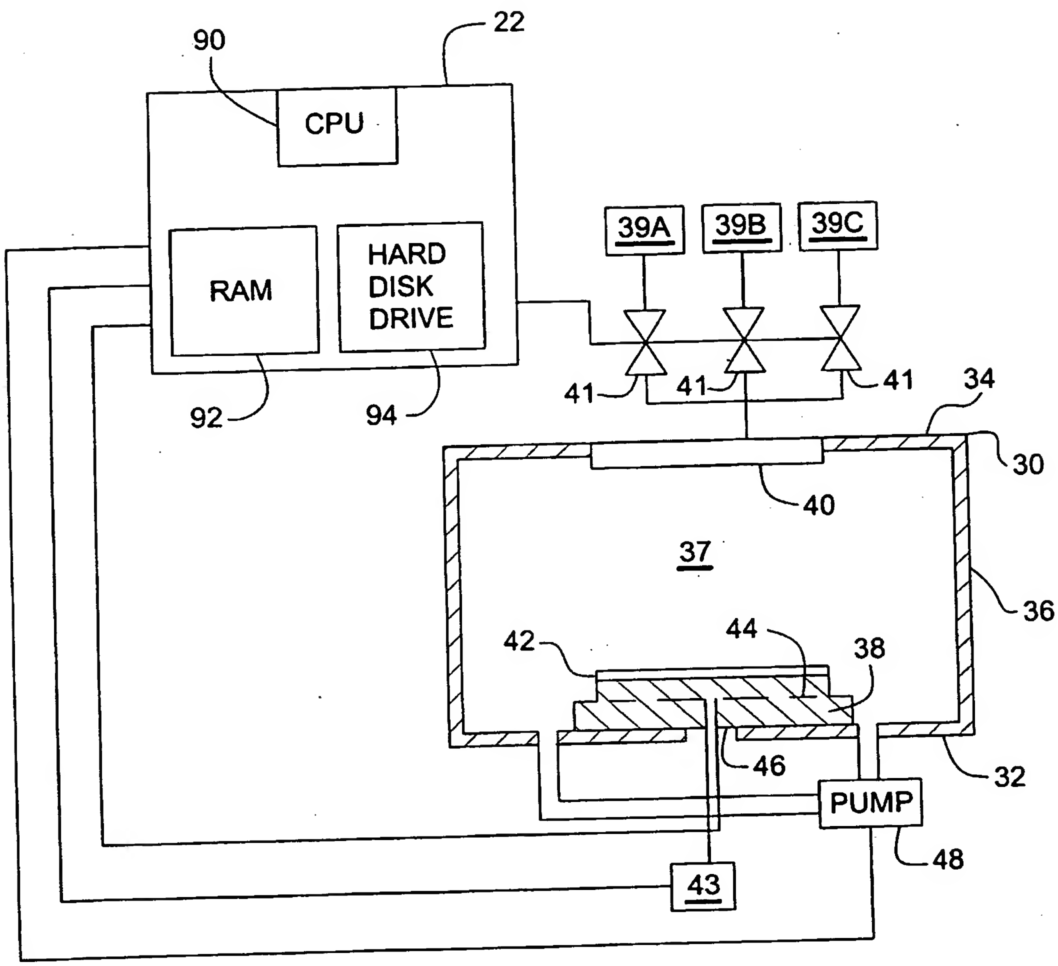


FIG. 1



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43

FIG. 2

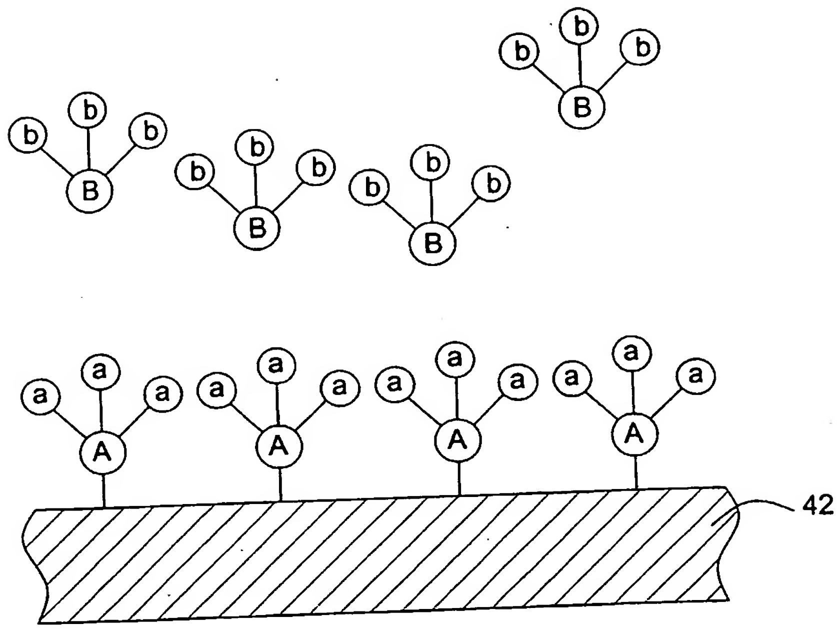


FIG. 3

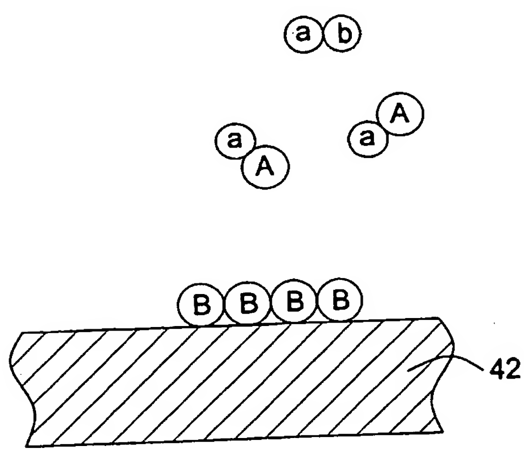
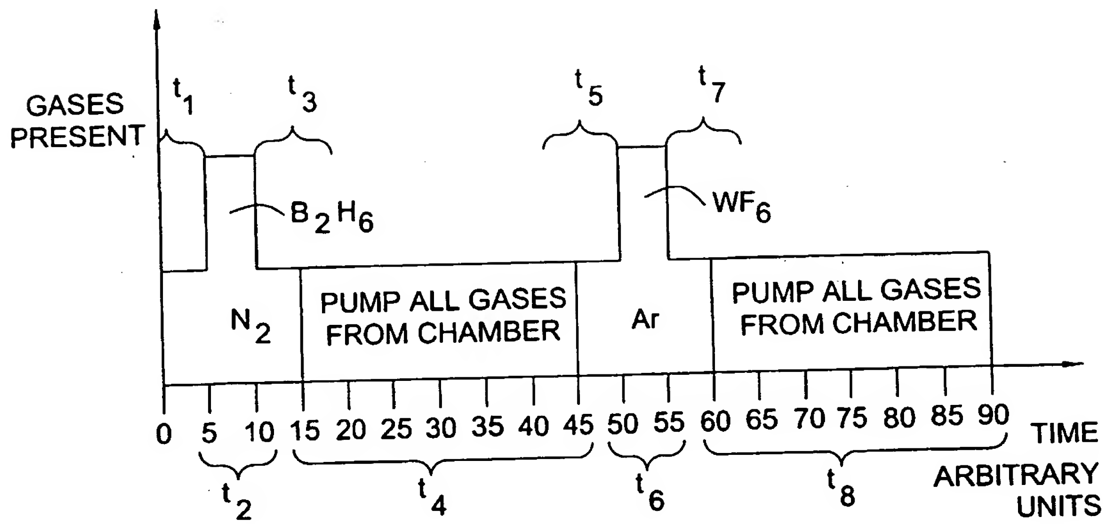


FIG. 4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t_5
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PUMP ALL GASES
FROM CHAMBER
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ARBITRARY
UNITS
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t_4
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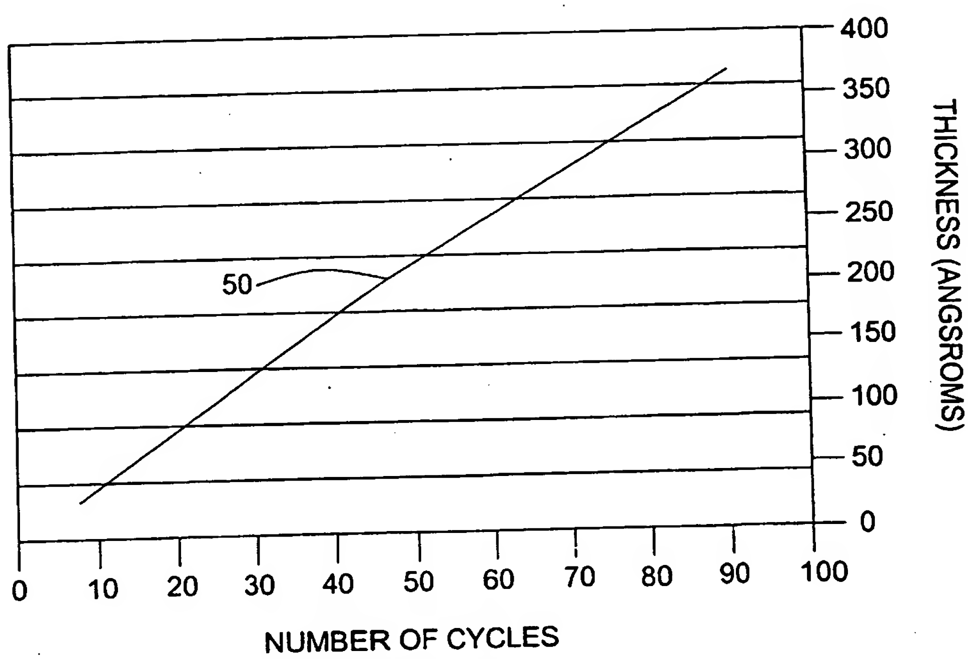
t_8

FIG. 5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NUMBER OF CYCLES

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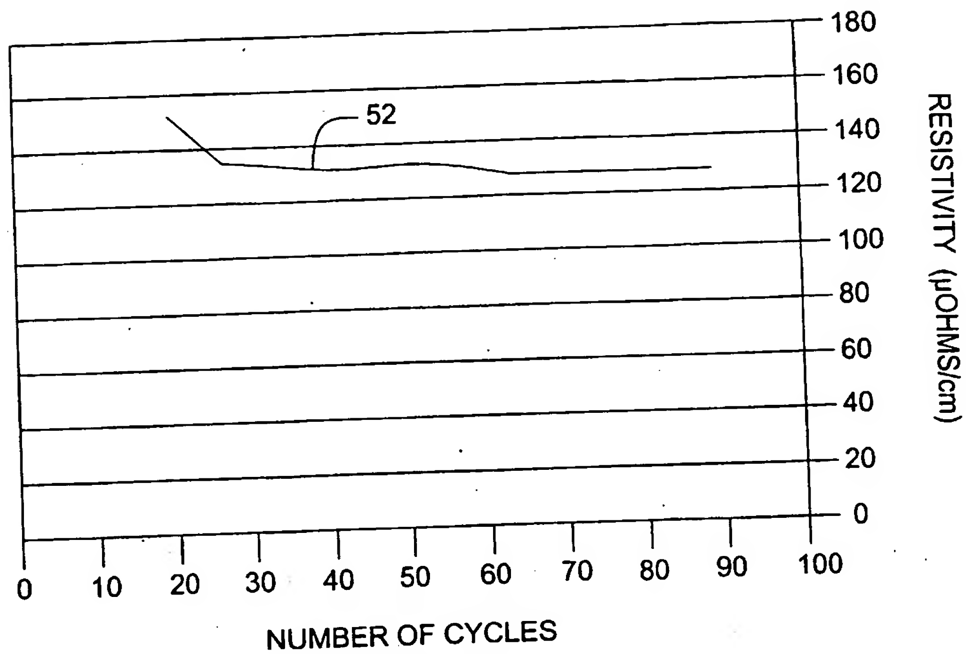
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90
100
NUMBER OF CYCLES

FIG. 7

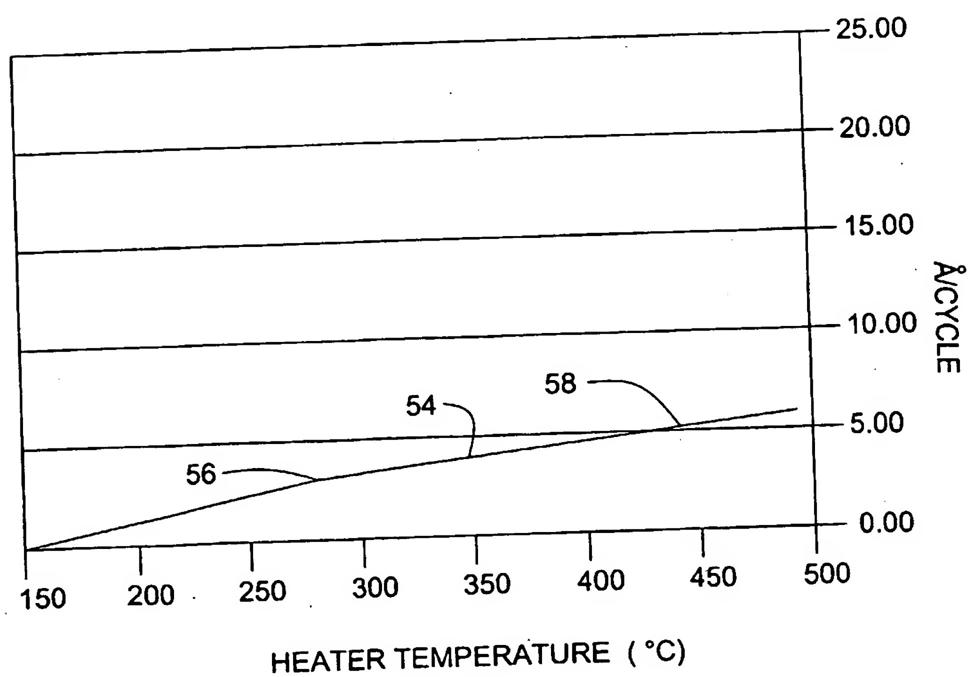
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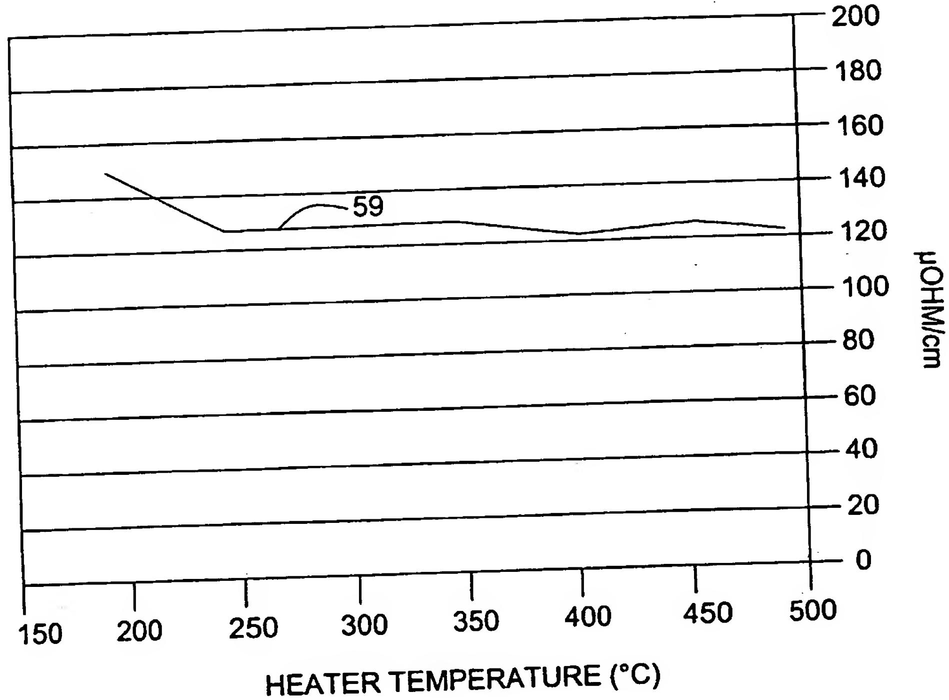
FIG. 8



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60
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μOHM/cm
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500
HEATER TEMPERATURE (°C)

FIG. 9

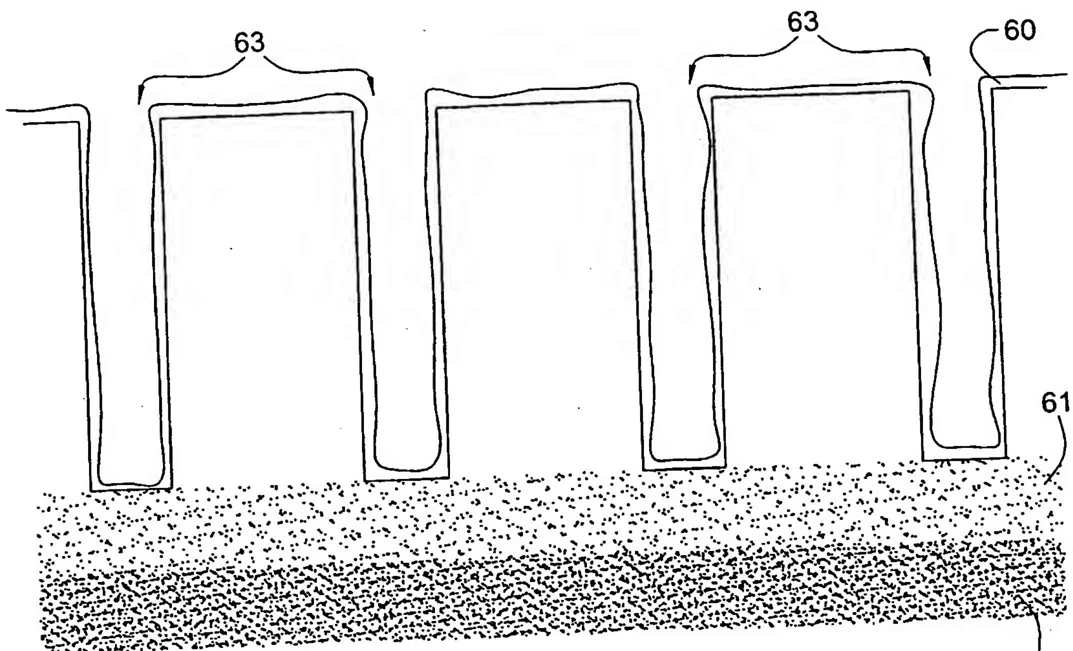


FIG. 10

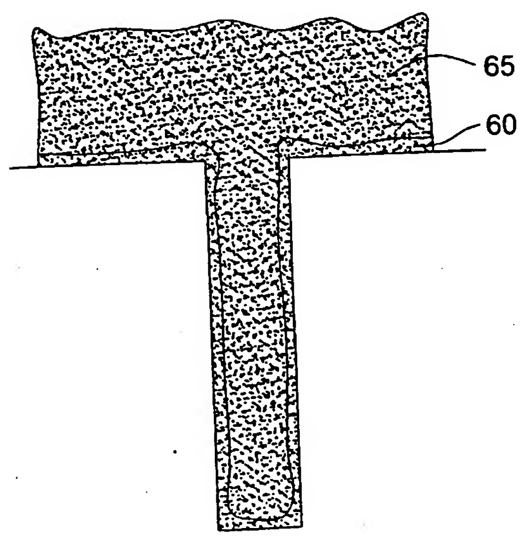
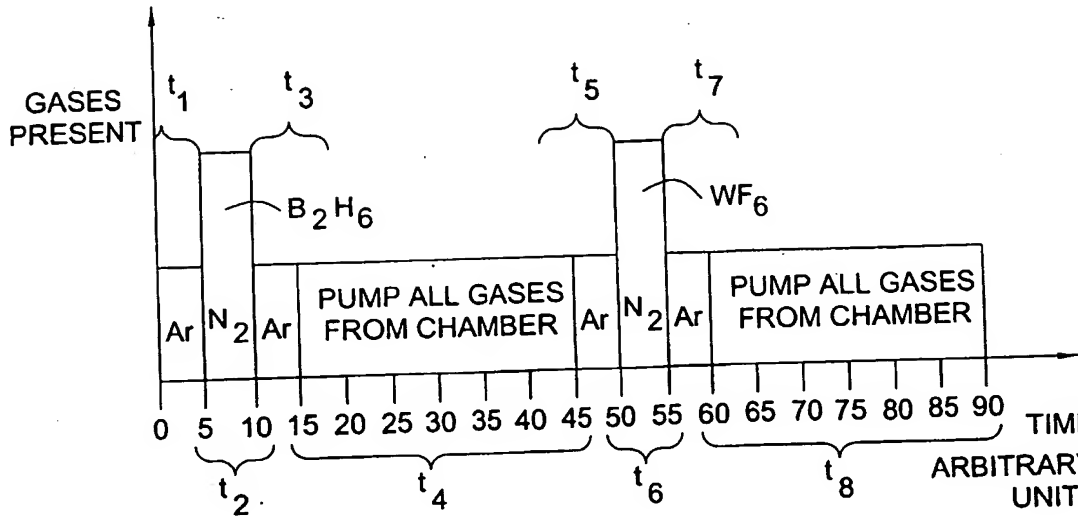


FIG. 11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N2
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N2
Ar
PUMP ALL GASES FROM CHAMBER
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TIME ARBITRARY UNITS
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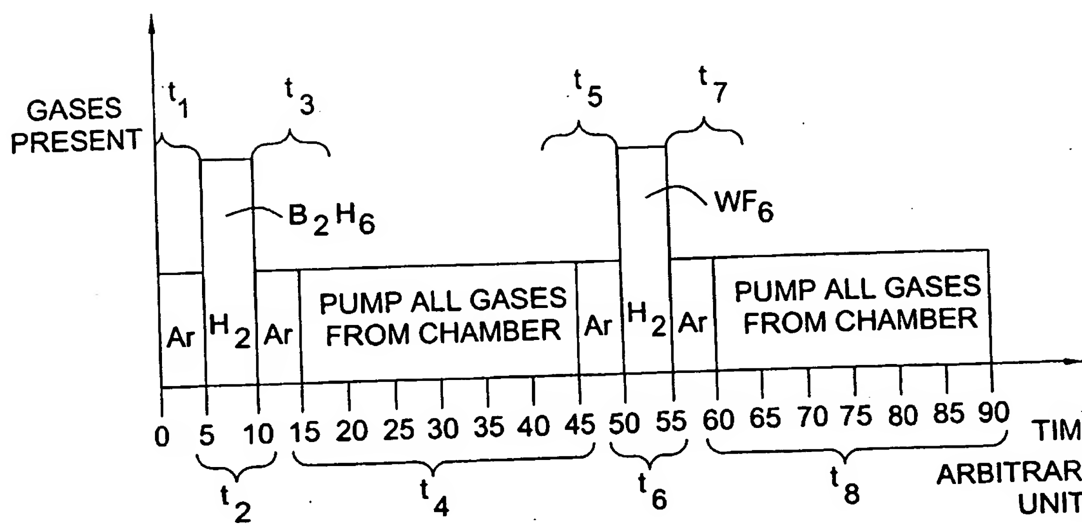
t4
t6
t8

FIG. 12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TIME ARBITRARY UNITS
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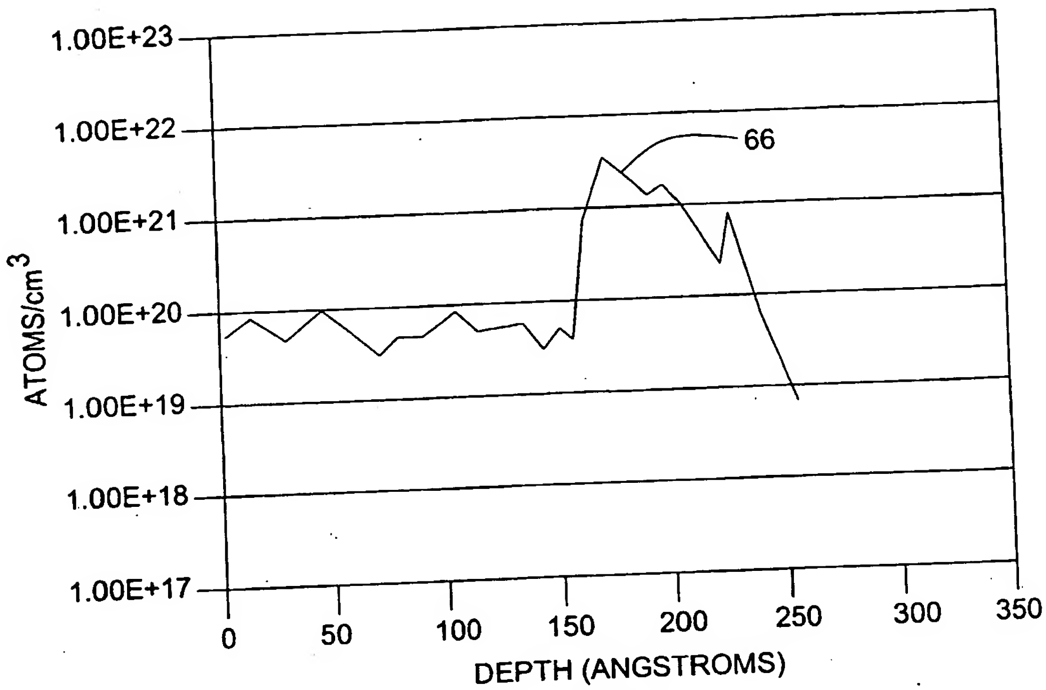
t6
t8

FIG. 13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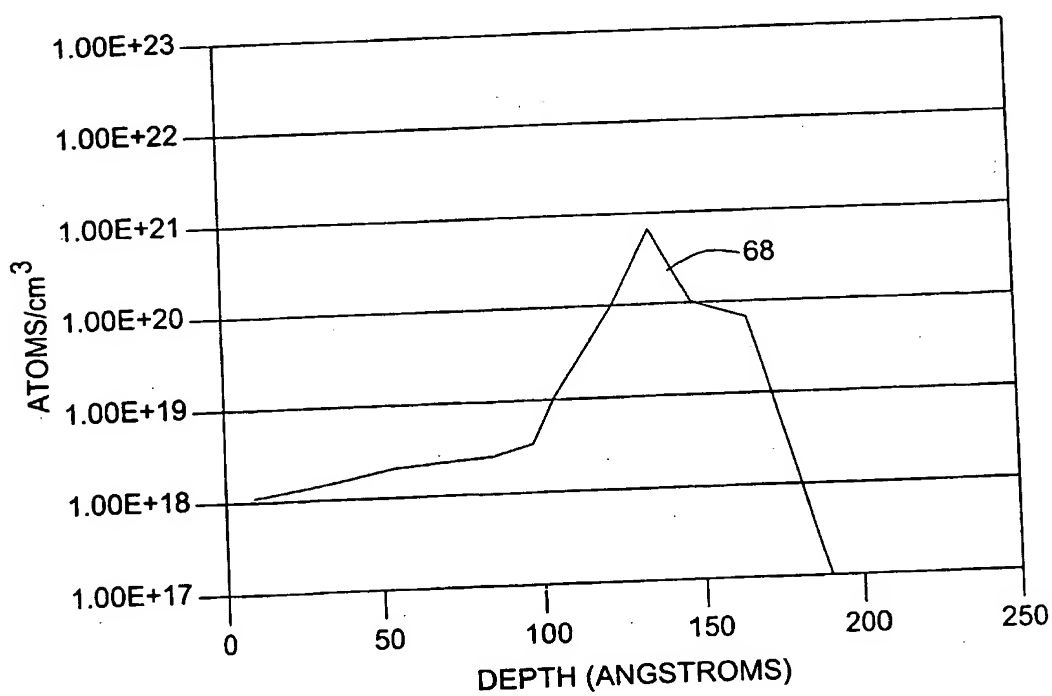
DEPTH (ANGSTROMS)

FIG. 14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DEPTH (ANGSTROMS)

FIG. 15

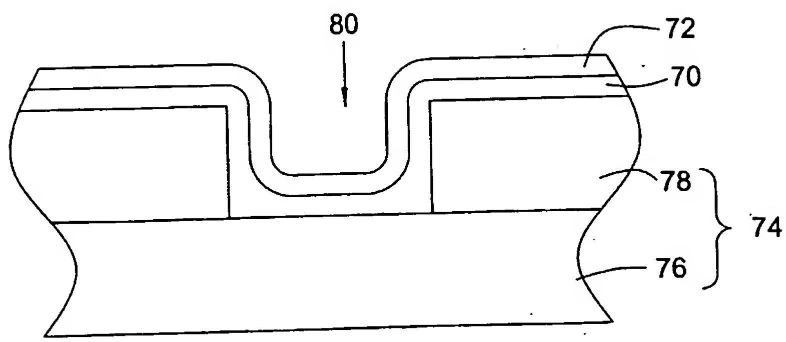

FIG. 16

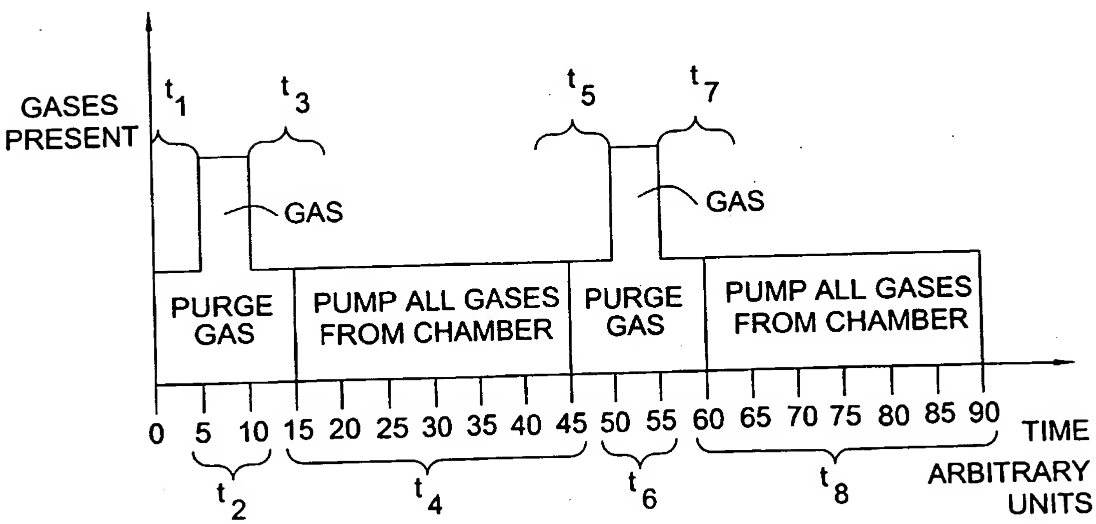

FIG. 17

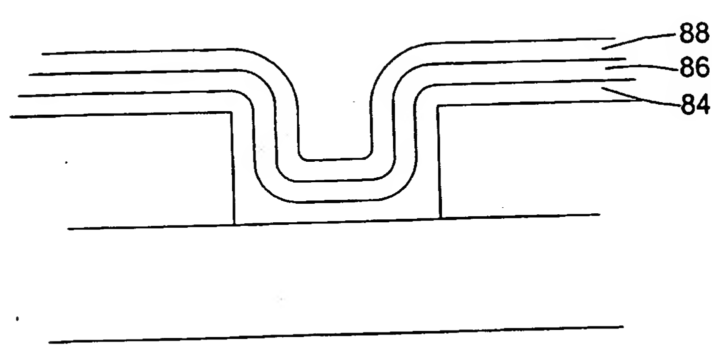

FIG. 18

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(19) World Intellectual Property Organization
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(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
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(71) Applicant (*for all designated States except US*): APPLIED MATERIALS, INC. [US/US]; 3050 Bowers Avenue, Santa Clara, CA 95054 (US).

(72) Inventor; and
(75) Inventor/Applicant (*for US only*): BYUN, Jeong, Soo [KR/US]; 20975 Valley Green Dr., Cupertino, CA 95014 (US).

(74) Agent: TACKETT, Keith, M.; Moser, Patterson & Sheridan, LLP, 3040 Post Oak Blvd., Suite 1500, Houston, TX 77056 (US).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

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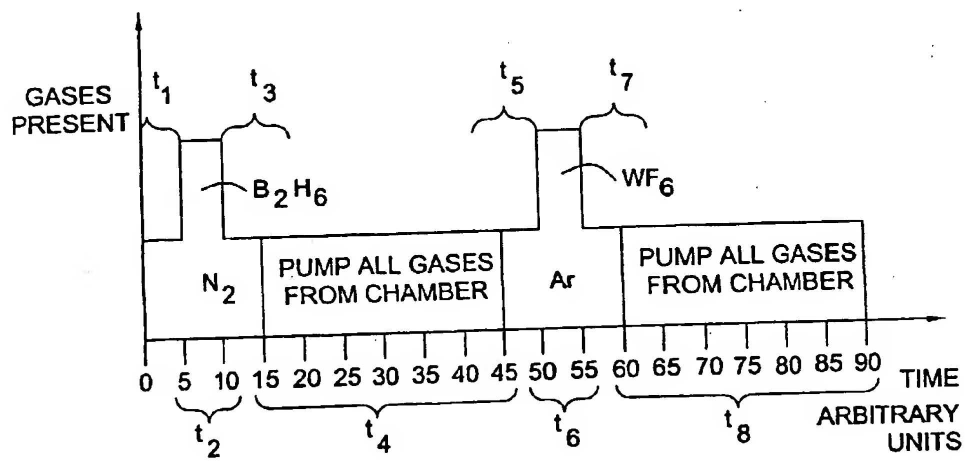
— *of inventorship (Rule 4.17(iv)) for US only*

Published:
— *with international search report*

(88) Date of publication of the international search report: 30 October 2003

[Continued on next page]

(54) Title: METHOD AND APPARATUS FOR DEPOSITING TUNGSTEN AFTER SURFACE TREATMENT TO IMPROVE FILM CHARACTERISTICS



(57) Abstract: A method and system to form a refractory metal layer over a substrate includes introduction of a reductant, such as PH3 or B2H6, followed by introduction of a tungsten containing compound, such as WF6, to form a tungsten layer. It is believed that the reductant reduces the fluorine content of the tungsten layer while improving the step coverage and resistivity of the tungsten layer. It is believed that the improved characteristics of the tungsten film are attributable to the chemical affinity between the reductants and the tungsten containing compound. The chemical affinity provides better surface mobility of the adsorbed chemical species and better reduction of WF6 at the nucleation stage of the tungsten layer. The method can further include sequentially introducing a reductant, such as PH3 or B2H6, and a tungsten containing compound to deposit a tungsten layer. The formed tungsten layer can be used as a nucleation layer followed by bulk deposition of a tungsten layer utilizing standard CVD techniques. Alternatively, the formed tungsten layer can be used to fill an aperture.

WO 03/009360 A3

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 02/22487

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 H01L21/285 H01L21/768

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 H01L C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	MICHAEL YANG ET AL: "Atomic Layer Deposition of Tungsten Films from WF6/B2H6" ADVANCED METALLIZATION CONFERENCE (AMC 2001); PROCEEDINGS OF THE CONFERENCE, MONTREAL, 8 - 11 October 2001, pages 655-660, XP008014661 the whole document ---	1-15
X Y	US 5 306 666 A (IZUMI HIROHIKO) 26 April 1994 (1994-04-26) the whole document ---	1,10-12, 14 2-9,13
	-/--	

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
6 March 2003	13/03/2003

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Ploner, G

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X Y	HERNER S B ET AL: "Homogeneous Tungsten Chemical Vapor Deposition on Silane Pretreated Titanium Nitride" ELECTROCHEMICAL AND SOLID-STATE LETTERS, IEEE SERVICE CENTER, PISCATAWAY, NJ, US, vol. 2, no. 8, August 1999 (1999-08), pages 398-400, XP000864981 ISSN: 1099-0062 the whole document	10,12,14 2-9,13
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A	PATENT ABSTRACTS OF JAPAN vol. 016, no. 283 (C-0955), 24 June 1992 (1992-06-24) & JP 04 074865 A (FUJITSU LTD), 10 March 1992 (1992-03-10) abstract	1-18

INTERNATIONAL SEARCH REPORT

Information on patent family members

Internati lication No
PCT/US 02/22487

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			EP	0981656	A1	01-03-2000
			JP	2001525889	T	11-12-2001
			TW	459063	B	11-10-2001
			WO	9851838	A1	19-11-1998
JP 04074865	A	10-03-1992	NONE			

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
30 January 2003 (30.01.2003)

PCT

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WO 03/009360 A3

(51) International Patent Classification[7]: H01L 21/285, 21/768

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(71) Applicant (*for all designated States except US*): **APPLIED MATERIALS, INC.** [US/US]; 3050 Bowers Avenue, Santa Clara, CA 95054 (US).

(72) Inventor; and
(75) Inventor/Applicant (*for US only*): **BYUN, Jeong, Soo** [KR/US]; 20975 Valley Green Dr., Cupertino, CA 95014 (US).

(74) Agent: **TACKETT, Keith, M.**; Moser, Patterson & Sheridan, LLP, 3040 Post Oak Blvd., Suite 1500, Houston, TX 77056 (US).

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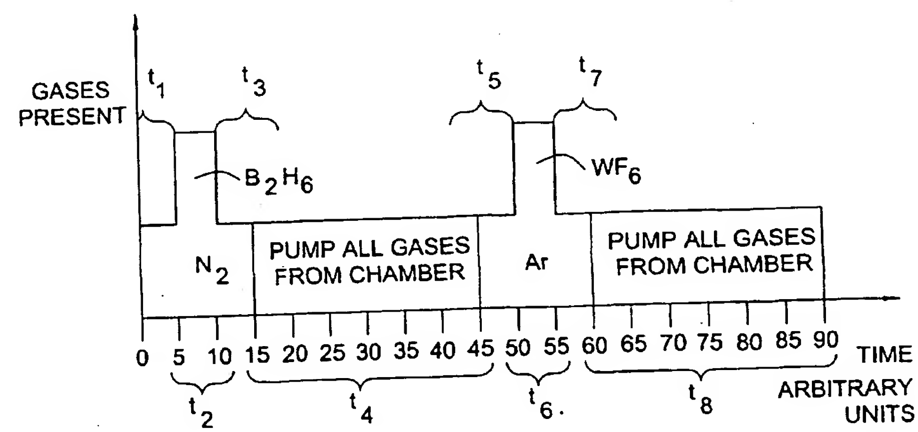
(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declaration under Rule 4.17:
— *of inventorship (Rule 4.17(iv)) for US only*

Published:
— *with international search report*
— *with amended claims*

[Continued on next page]

(54) Title: METHOD AND APPARATUS FOR DEPOSITING TUNGSTEN AFTER SURFACE TREATMENT TO IMPROVE FILM CHARACTERISTICS



(57) Abstract: A method and system to form a refractory metal layer over a substrate includes introduction of a reductant, such as PH3 or B2H6, followed by introduction of a tungsten containing compound, such as WF6, to form a tungsten layer. It is believed that the reductant reduces the fluorine content of the tungsten layer while improving the step coverage and resistivity of the tungsten layer. It is believed that the improved characteristics of the tungsten film are attributable to the chemical affinity between the reductants and the tungsten containing compound. The chemical affinity provides better surface mobility of the adsorbed chemical species and better reduction of WF6 at the nucleation stage of the tungsten layer. The method can further include sequentially introducing a reductant, such as PH3 or B2H6, and a tungsten containing compound to deposit a tungsten layer. The formed tungsten layer can be used as a nucleation layer followed by bulk deposition of a tungsten layer utilizing standard CVD techniques. Alternatively, the formed tungsten layer can be used to fill an aperture.

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

AMENDED CLAIMS

[Received by the International Bureau on 13 May 2003 (13.05.03);
original claims 1-18 replaced by amended claims 1-32 (5 pages)]

1. A method of forming a tungsten layer over a substrate in a processing chamber, comprising:

forming a tungsten nucleation layer, comprising:

sequentially introducing pulses of a reductant selected from a group including PH_3 and B_2H_6 and pulses of a tungsten containing compound; and

introducing a purge gas at least partially between the pulses of the reductant and the pulses of the tungsten containing compound.

2. The method of claim 1, wherein the reductant comprises B_2H_6.

3. The method of claim 1, wherein the substrate comprises a titanium-containing layer and the tungsten nucleation layer is formed over the titanium-containing layer.

4. The method of claim 3, wherein the titanium-containing layer is selected from a group including Ti and TiN.

5. The method of claim 3, wherein the titanium-containing layer is formed by sequential deposition.

6. The method of claim 1, further comprising forming a bulk tungsten layer over the nucleation layer.

7. The method of claim 6, wherein the bulk tungsten layer is formed over the tungsten nucleation layer by sequential deposition.

8. The method of claim 6, wherein the bulk tungsten layer is formed over the tungsten nucleation layer by chemical vapor deposition.

9. The method of claim 6, wherein the tungsten nucleation layer and the bulk tungsten layer are formed in the same processing chamber.

10. The method of claim 6, wherein the tungsten nucleation layer and the bulk tungsten layer are formed in separate processing chambers.

11. The method of claim 6, wherein the tungsten nucleation layer and the bulk tungsten layer are formed using the same reducing agent.

12. The method of claim 6, wherein the tungsten nucleation layer and the bulk tungsten layer are formed using different reducing agents.

13. A method of forming a tungsten layer over a substrate in a processing chamber, comprising:

presoaking the substrate with a presoak compound selected from a group including PH_3 or B_2H_6 to form a presoak layer of the presoak compound over the substrate;

forming a tungsten layer over the presoak layer by sequentially introducing pulses of a reductant and pulses of a tungsten containing compound.

14. The method of claim 13, wherein the substrate is presoaked and the tungsten layer is formed in the same processing chamber.

15. The method of claim 13, wherein the reductant is selected from a group including PH_3 and B_2H_6.

16. The method of claim 13, wherein the reductant and the presoak compound comprise B_2H_6.

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17. The method of claim 13, further comprising introducing a purge gas at least partially between the pulses of the reductant and the pulses of the tungsten containing compound.

18. The method of claim 13, wherein the substrate comprises a titanium-containing layer and the presoak layer is formed over the titanium-containing layer.

19. The method of claim 13, wherein the tungsten layer comprises a tungsten nucleation layer.

20. The method of claim 19, further comprising forming a bulk tungsten layer over the tungsten nucleation layer.

21. A processing system for a substrate comprising:

a first processing chamber, comprising:

a body;

a holder disposed within the body to support the substrate;

a gas delivery system in fluid communication with the body; and

a controller in electrical communication with the gas delivery system; and

a memory in data communication with the controller, the memory comprising a computer-readable medium having a computer-readable program embodied therein, the computer readable program including a set of instructions for forming a tungsten nucleation layer over the substrate by sequentially introducing pulses of a reductant selected from a group including PH_3 and B_2H_6 and pulses of a tungsten containing compound and by introducing a purge gas at least partially between the pulses of the reductant and the pulses of the tungsten containing compound.

22. The processing system of claim 21, wherein the computer readable program of the first processing chamber further comprises a second set of instructions to presoak the substrate prior to forming a tungsten nucleation layer.

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23. The processing system of claim 21, wherein the computer readable program of the first processing chamber further comprises a second set of instructions to form a bulk tungsten layer over the tungsten nucleation layer.

24. The processing system of claim 21, further comprising

a second processing chamber, comprising:

a body;

a holder disposed within the body to support the substrate;

a gas delivery system in fluid communication with the body;

wherein the controller is in electrical communication with the gas delivery system of the second processing chamber and wherein the memory is in data communication with the controller, the computer readable program including a second set of instructions for forming a bulk tungsten layer over the tungsten nucleation layer.

25. A method of forming a tungsten feature over a substrate in a processing chamber, comprising:

presoaking the substrate with B_2H_6 to form a presoak layer of B_2H_6 over the substrate;

forming a tungsten nucleation layer over the presoak layer by sequentially introducing pulses of B_2H_6 and pulses of a tungsten containing compound; and

forming a bulk tungsten layer over the tungsten nucleation layer.

26. The method of claim 25, wherein the bulk tungsten layer is formed over the tungsten nucleation layer by chemical vapor deposition.

27. The method of claim 26, wherein the bulk tungsten layer is formed over the tungsten nucleation layer by chemical vapor deposition utilizing silane and a tungsten containing compound.

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28. The method of claim 27, wherein the tungsten nucleation layer and the bulk tungsten layer are formed in separate processing chambers of a common processing system.

29. The method of claim 28, wherein the presoak layer and the tungsten nucleation layer are formed in the same processing chamber.

30. The method of claim 25, wherein the presoak layer is formed over a titanium-containing layer.

31. A method of forming a tungsten layer over a substrate in a processing chamber, comprising:

sequentially introducing pulses of a reductant with a hydrogen carrier gas, the reductant selected from a group including PH_3 and B_2H_6 and pulses of a tungsten containing compound; and

introducing a purge gas at least partially between the pulses of the reductant and the pulses of the tungsten containing compound.

32. The method of claim 31, wherein the purge gas comprises hydrogen gas.